

utilises a chelating agent to reduce the catalysts tendency to non-selectively decompose the hydrogen peroxide oxidant used. EP 0 385 631 A1 describes an oxidation process for the conversion of olefins to glycols utilising oxygen and carbon dioxide as reactants under supercritical conditions. A heterogeneous copper containing catalyst is proposed. U.S. Pat. No. 5,646,314 proposes performing the oxidation reaction in the presence of nonbasic salts in order to improve selectivity.

Furthermore it has long been recognised that metal containing zeolite catalysts rapidly become deactivated in use. There have been a number of methods developed to counter this deactivation and/or to regenerate the catalyst after use. U.S. Pat. No. 5, 741, 749 proposes a the regeneration of a titanium containing molecular sieve oxidation catalyst by treatment with a gas stream comprising specific amounts of molecular oxygen. WO 98/18555 proposes the regeneration of a titanium silicalite catalyst with a liquid solution of an oxidising agent. WO 98/ 18556 proposes the regeneration of a titanium silicalite catalyst under a specific gas flow

In US 5 210 336 a process is described for the conversion of olefins to glycols utilising a CuI/Cu₂O catalyst. The reaction is undertaken in the presence of carbon dioxide which acts as a solvent and a co-reactant, under supercritical conditions.

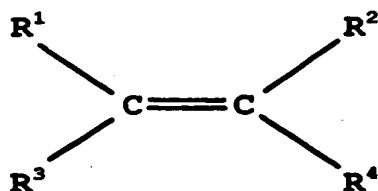
There are a number of problems with the processes of the prior art. Conversions and selectivities for the various reactions are in general still low or require additional process modifications which incur additional

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costs. Frequently the catalyst systems utilised require special treatments and/or frequent regeneration in order to maintain catalyst activity.

- 5 It has been surprisingly found that the conversion and selectivity of oxidation processes, in particular the

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wherein R^1 , R^2 , R^3 , and R^4 are the same or different and are selected from the group consisting of hydrogen and C_1 - C_8 alkyl (selected so that the total number of carbons in the olefin does not exceed 30).

The process of this invention is also suitable for use in epoxidizing olefins containing functional groups other than aliphatic hydrocarbyl moieties. For example, the carbon-carbon double bond can be substituted with groups such as $-\text{CO}_2\text{H}$, $-\text{CO}_2\text{R}_1$, $-\text{CN}$, or $-\text{OR}$ wherein R is an alkyl, cycloalkyl, aryl or aralkyl substituent. The radicals R^1 , R^2 , R^3 , and R^4 in the structural formula shown hereinabove may contain aryl, aralkyl, halo, nitro, sulfonic, cyano, carbonyl, (e.g. ketone, aldehyde,) hydroxyl, carboxyl (e.g ester, acid) or ether groups. Examples of olefins of these types include allyl alcohol, styrene, allyl chloride, allyl methyl ether, allyl phenyl ether, methyl methacrylate, acrylic acid, methyl acrylate, and stilbene.

The amount of hydrogen peroxide relative to the

minor amounts of boron, iron, and aluminum may be present.

Titanium silicalite catalysts suitable for use in the process of this invention will generally have a composition corresponding to the following empirical formula $x\text{TiO}_2:(1-x)\text{SiO}_2$, where x is between 0.0001 and 0.500. More preferably, the value of x is from 0.01 to 0.125. The molar ratio of Si:Ti in the lattice framework of the titanium silicalite is advantageously from 9.5:1 to 99:1 (most preferably, from 9.5:1 to 60:1). The use of relatively titanium-rich silicalites may also be desirable. The preferred catalyst is titanium silicalite-1. One form of catalyst suitable for use in the process of the present invention is a "cherry type" catalyst which consists of a core of material e.g. silica/alumina and a shell of different material e.g. silica/titania as described for example in EP 634 212. The titanium silicalite catalyst may be incorporated in or in the form of a membrane; for example TS-1 or Ti-MCM-41 may be occluded in polydimethylsiloxane (PDMS) membranes, as described in Chemical Communications (1997) pages 137 to 138.

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a particularly short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration of organic solvent as well as catalyst activity and the type of reactor or reaction system (i.e. batch vs continuous) employed. In a batch-type or slurry reaction, for example, the amount of catalyst will

desired degree of conversion, the epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, or crystallisation. After separating from the epoxidation reaction mixture by any suitable method such as filtration (as when a slurry reactor is utilised, for example), the recovered titanium silicalite catalyst may be economically re-used in subsequent epoxidations. Where the catalyst is deployed in the form of a fixed bed, the epoxidation product withdrawn as a stream from the epoxidation zone will be essentially catalyst free with the catalyst being retained within the epoxidation zone. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled or otherwise disposed of. In certain embodiments of the instant process where the epoxide is produced on a continuous basis, it may be desirable to periodically or constantly regenerate all or a portion of the used catalyst in order to maintain optimum activity and selectivity. Suitable regeneration techniques are well-known and include, for example, calcination and solvent treatment. Such regeneration and/or treatment may not be necessary until a significant number of recycles have occurred through the process of the present invention. Typical examples of suitable regeneration methods are provided in WO99/01445, WO98/18556, WO98/28072 and Journal of Molecular Catalysis A:Chemical 117 (1997) 351-356. The disclosures of each of these references are incorporated by reference.

The present invention is further illustrated by means of the following examples:

Example 1

A TS-1 catalyst (prepared by the procedure given in Applied Catalysis, 99, (1993), pages 71-84) was utilised in the oxidation of 1-octene to 1,2-epoxyoctane with and without supercritical carbon dioxide as the solvent. A 250 cm³ batch autoclave equipped with a temperature controller, mechanical stirrer (1000 rpm), reagents feed line, sampling line and vent line was charged in two separate experiments with the following reagents.

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Reagents	Experiment 1	Experiment 2
	Weight (g)	Weight (g)
1-octene	14.52	7.26
H ₂ O ₂ (30wt% in H ₂ O)	0.44*	0.22*
Methanol	112.5	56.25
Carbon Dioxide	0	74.2
TS-1 catalyst	1.0	0.5
Total	128.46	138.43

*= the weight of H₂O₂ does not include the weight of H₂O

For Experiment 1 the reaction was undertaken at 65°C for 60 minutes. For Experiment 2 the reactor was first pressurised with carbon dioxide gas to 48 bar (48 x 10⁵ Nm⁻²), after which 74.2g of liquid carbon dioxide was

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